FIFTY YEARS OF METALS THEORY

by Walter A. Harrison

ABSTRACT

Metallic properties have been attributed to free electrons almost since the discovery of the electron in 1897. This became a theory of metals when Bloch and Sommerfeld applied quantum theory to these electrons in 1928, providing the basis for the subsequent development of the theory. That development was, however, not by a direct process of deduction, but it required genuinely new concepts in order to become simple and understandable. Four such concepts are discussed here: the quasi-particle state of the electron, the representation of its strong interaction with the atoms by a weak pseudopotential, the formation of a local magnetic moment by itinerant electrons, and the superconducting order through which the electrons produce the superconducting state.

I. INTRODUCTION

Just over fifty years ago Felix Bloch published his thesis work on the theory of metals.[1] Viewing from that vantage point, one might feel that the essential problem had been solved and it remained only to work out the detailed consequences. The truth was more that a foundation had been laid upon which a major edifice was to be created. To be sure, many details have been worked out, but I will not discuss them here; I will focus on a series of genuinely new concepts or points of view that were required as the theory moved forward. I begin by describing the status of the theory fifty years ago and noting the signs that were present suggesting undiscovered treasures. We will then see just what some of those treasures turned out to be.

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The understanding of the properties special to metals began near the turn of the century soon after the electron was discovered by J. J. Thomson.[2] Drude[3] suggested that we could explain immediately some of the most conspicuous properties of metals—their shiny luster and their ability to conduct electricity and heat—if we would assume that the electrons moved freely within a metal and were in thermal equilibrium with the metallic atoms. When Lorentz[4] worked out the consequences of this assumption in the next few years, however, he was led to two serious difficulties. First, the laws of gases required that such an electron gas would need a definite and well-determined amount of energy to raise its temperature—and experiments clearly showed that electrons in metals required very much less. Second, the decreasing resistivity of metals with decreasing temperature required that the electrons must be able to travel increasingly large distances through the metal without colliding with the atoms as the temperature was decreased; there was no basis for this within the theory and indeed it seemed quite implausible. These contradictions remained for some twenty-five years until the arrival of quantum theory.

In a sense the theoretical situation worsened in the interim because of a new experimental development. Onnes[5] explored the behavior of the conductivity of metals at extremely low temperatures to see if indeed the path lengths for the electrons continued to lengthen, with a continuing decrease in resistivity, or whether the electron gas might condense out like frost from the air, giving an increasing resistivity. These two possibilities are illustrated in figure 1. He found that neither was correct. At a critical temperature, T_c, the conductivity surprisingly dropped to exactly zero. We will return later to this remarkable "superconductivity," which remained a mystery for nearly fifty years and was a continual reminder that the theory of metals was not finished.

Quantum mechanics developed in the mid-twenties and immediately the two difficulties raised by Lorentz were resolved. Sommerfeld[6] used the quantum-mechanical statistics for electrons to show that they should *not* absorb energy like a classical gas, and Bloch[1] showed that in a perfect crystal the wave-like electrons of quantum theory could propagate over as long a distance as one wished through the metal. The electron state $|\psi_{\mathbf{k}}>$ could be written as what is now called a *Bloch function*,

$$\psi_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r})\, e^{i\mathbf{k}\cdot\mathbf{r}} \tag{1}$$

where the factor $e^{i\mathbf{k}\cdot\mathbf{r}}$ describes the propagation of a free electron of wave number $\mathbf{k}$ and the factor $u_{\mathbf{k}}(\mathbf{r})$, which it modulates, has the full translational symmetry of the crystal. It was only with disruptions of the perfection of the crystal, which increase with increasing temperature, that the factors become mixed, the electrons are deflected, and the metal becomes resistive.

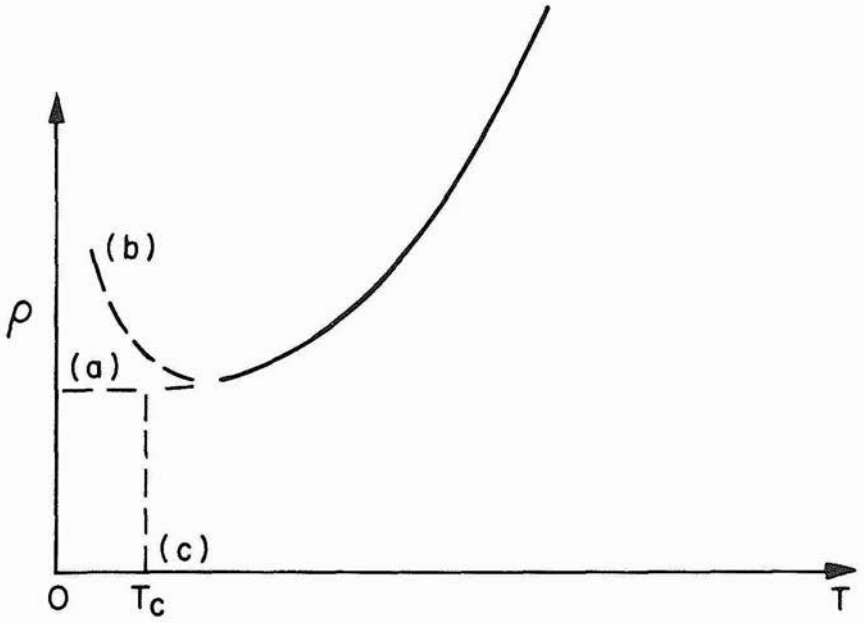

FIG. 1. ONNES IN 1911 MEASURED THE RESISTIVITY ϱ of metals to very low temperature to see if a) it would continue to decrease, or b) it would reach a minimum and increase as the electrons froze out on the atoms. He found instead that, at least for mercury, c) the resistance suddenly dropped to zero, forming a superconducting state.

This finding not only resolved the earlier difficulties, but laid out a path to be followed for the detailed understanding of metals and, in fact, non-metallic solids: One must determine the energies of these wave-like Bloch states of the electrons, and most of the properties of the metals should be understandable in terms of them. Indeed, within the next few years a very extensive theory of metals developed, as reflected in texts by Mott and Jones[7] and by Wilson[8] in 1936.

The theory remained essentially unchanged for the next twenty years, largely because of World War II. In the fifties a number of workers took up the path implicitly laid down in Bloch's work. The newly invented electronic computers allowed the direct theoretical determination of the Bloch states and their energies, studies which are called "energy band calculations." There were still uncertainties as to how these should be carried out, but at the same time pure materials became available and ingenious experimental techniques were developed so that experimental tests could be made of any proposed approximations. This confrontation of experiment and the emerging theory centered on geometrical representations of the directly measurable aspects of the energy bands. These so-called "Fermi surfaces"

are characteristic of each metal.[9] By now the Fermi surfaces, and indeed the complete energy bands, are known in some detail for almost all pure metals. The same theoretical techniques should provide the same information for alloys or imperfect crystals and are limited only by the complexity of the systems one is willing to consider.

Such a broad-brush picture of the theory of metals would suggest that there were two great bursts: One followed the discovery eighty years ago of the electron as we learned the consequences of assuming that the electron in the metal was subject to the classical laws of mechanics and statistical mechanics. The second followed the development fifty years ago of the quantum mechanics and quantum statistics that, in fact, describe the behavior of electrons. If we look more closely at the past fifty years we see that a number of additional genuinely new concepts were required, each followed by its own careful exploration. It is these new concepts in the past fifty years that I wish to discuss, rather than the very impressive consequences that have derived from them. This then is a study of the development of a field of science in which the fundamental laws appeared to be known.

I have implicitly made a distinction between two kinds of new concepts in science: creations, such as the invention of quantum theory, and discoveries of existing entities, such as electrons. We see in the theory of metals that both kinds of steps are necessary and there seems to be a sharp distinction between them. We should consider the difference more closely.

Perhaps a very simple example of invention in a known field would be helpful. We might seek the description of the motion of a string of beads hurled through the air or through a vacuum, as illustrated in figure 2. If we

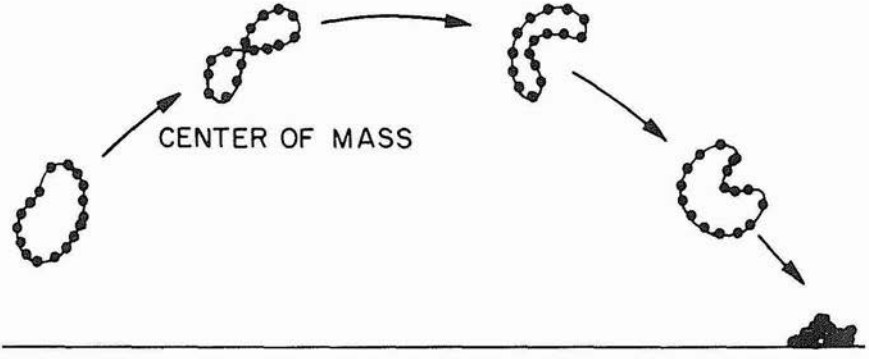

FIG. 2. THE DYNAMICAL LAWS GOVERNING THE TRAJECTORY of a string of beads are known, as are the laws that govern electrons in metals. Simultaneous solution of the equations of motion for each bead is a correct procedure, but the concept of the "center of mass" allows one easily, and reasonably accurately, to predict where the necklace will land.

specify the velocity of each bead at the beginning of the trajectory, we may calculate the forces of the beads on each other and the gravitational force on each and could calculate the subsequent motion; the laws of the dynamics are known. However, we might invent or define the *center of mass* of the necklace. We may immediately then show that the motion of the center of mass is very simple, and by considering just its motion we may be able to calculate on the back of an envelope where the necklace will land. We have given up some accuracy in doing this, since we do not tell just where each bead lands, but if the necklace has been thrown a long way, it may be enough to know where the necklace as a whole hits the ground. Without that invention, the solution of the equations of motion for each of the beads would have required a sizable computer. The concept of "center of mass" was never necessary to the solution of the problem, but its definition was necessary to extract the simplicity from an intrinsically complex situation.

One could argue, on the other side, that a concept such as the center of mass (or the other concepts I will discuss) so naturally and simply describes the physical world that if one person did not invent it someone else would. In this sense the invention is essentially a discovery of a concept waiting to be found. It may be a semantic point of distinction, but I hope the illustration does clarify the parts of the theory I wish to discuss.

Before beginning, I should note where the necessity of the new concepts could be spotted in the early theory. I noted that Bloch's theorem about the motion of the electrons depended upon the perfect crystalline symmetry of the metallic lattice, but Mott[7] noted very early that the resistivity of most metals does not change greatly upon melting, at which time this periodicity is lost altogether. Bloch's theorem is unquestionably true, but is there some more general reason that applies to much more general systems? Furthermore, the Bloch states were derived by consideration of a single electron moving through the metal. Any estimate would suggest that the electrons in metals are in continual contact with each other (through their electrostatic interaction) like marbles in a bag or molecules in a liquid; how can we then describe them as moving in independent trajectories through the metal? Indeed, when Bloch and others went on to describe detailed properties of ferromagnetic metals, they thought of the electrons as little magnets attached to individual atoms, as if they had frozen out, as Onnes speculated. This was quite inconsistent with the original Bloch states. How can the two views be reconciled? Finally, there was the problem of superconductivity, which remained outside the domain of respectable theory of metals and was scarcely mentioned in the earlier texts.[7,8] We will consider concepts that in some sense made these very difficult problems simple.

II. THE ELECTRON-ELECTRON INTERACTION

It is good to begin with the problem of the mutually interacting gas of electrons in a metal, which is truly an insoluble problem, though the needed fundamental laws are precisely known. It is well known in classical physics that one can solve generally for the motion of two interacting particles, but not for three. For three particles one must resort to numerical or approximate methods. The same is true in quantum mechanics, and with a typical metal crystal containing 10^{22} electrons, the direct numerical methods are out of the question and approximational techniques need to be developed. This branch of physics is called "many-body physics" and is concerned with other problems as well. I would like to describe an approach to the problem that transcends the detailed solution, much as the center of mass did for the beads. L. D. Landau,[10] in the Soviet Union, suggested that we should first imagine a system of particles (electrons) that did not interact with each other at all. Then each electron would have a well-defined wave number. We represent the states by a wave number as in Eq. (1), though Landau was not concerned about the effect of the crystal potential. He therefore regarded $u_{\mathbf{k}}(\mathbf{r})$ in Eq. (1) as a constant. In this case $\mathbf{k}$ becomes the momentum divided by Planck's constant, $\mathbf{k}=\mathbf{p}/\hbar$, which would not change because the electron did not interact with any other electrons. The state of the entire system could be given by listing (for each of the two possible electron spin orientations) all possible wave numbers, indicating whether or not an electron occupied each corresponding state; i.e., we give the function $n(\mathbf{k})$, with $n=1$ if the state is occupied and $n=0$ if it is not. (We let $n(\mathbf{k})$ represent the occupation of both spin states.) Landau then asserted that even if the electrons interact with each other, the resulting state of the interacting system can again be completely specified by an $n(\mathbf{k})$, which he called the occupation of *quasiparticle* states. It follows that the total energy of the system of real electrons is a *functional* of the function $n(\mathbf{k})$; that is, $E\{n(\mathbf{k})\}$. Thus he asserted that the entire effect of the interactions was to replace the freely propagating electron by a quasiparticle consisting of the electron and a "wake," which it carries with it as it moves through the sea of other electrons. Then the quantity in the interacting system that plays the role of the electron energy in the noninteracting system is the quasiparticle energy $\epsilon_{\mathbf{k}}$ defined as the change of the total energy when an electron is added in the quasiparticle state $|\mathbf{k}>$:

$$\epsilon_{\mathbf{k}} = \delta E\{n(\mathbf{k})\}/\delta n(\mathbf{k}) \tag{2}$$

The interactions affect the energy and the velocity of the quasiparticle, but these changes might be obtained from experiment, and the concept allowed us to continue to think simply about an intrinsically complex, and in fact

insoluble, problem.

When this theory reached the West (there was a delay of some years because translations were not made routinely during the Cold War), it was regarded as a rather bold, and perhaps unjustified, assumption. Efforts were initiated to see if the Fermi liquid theory could be derived from the rigorous and powerful "quantum field theories," which had been developed here and which were the basis of many-body physics in the West. Landau's response was interesting; he thought it would be a nice test of the expansions used in quantum field theory. This was not the outrageous comment it might at first seem. Quantum field theory began with the noninteracting electrons and systematically corrected for the interaction. It necessarily, therefore, led to a state of the system that could be specified completely by giving the $n(\mathbf{k})$ of the zero-order (noninteracting) state and therefore satisfied Landau's starting assumption. Landau might conceivably have been wrong with his Fermi liquid theory, but if so the perturbation theory used in quantum field theory was necessarily also inapplicable. We will see that both are inapplicable in superconducting metals.

One thing Fermi liquid theory could *not* do, which field theory could, was predict the size of the corrections to energy and velocity for the quasiparticles. It was difficult, but efforts by theorists to calculate the corrections, along with concurrent experimental studies of metals, made clear that the dynamical properties of the quasiparticles were only slightly different from those of noninteracting electrons, and the independent-electron view used by Bloch was justified. This did not solve all of the problems. Even if electrons could be studied one at a time, we must know how to approximate the potential they move in if we are to determine the electron (or quasiparticle) states and energies. Procedures for constructing these have come through hard work and experience.

III. ELECTRON-ATOM INTERACTIONS

I turn next to the interactions between the individual electronic quasiparticles and the atoms that make up the crystal, and why they can travel so far in the metal even if the crystalline symmetry necessary to Bloch's theorem is absent. Before it was understood why there was such a small change in resistivity when a metal melted, it was learned that the energies of the Bloch states in perfect crystals were very little different from what they would be if the electrons could move completely freely through the metal, as Drude had originally assumed. This had been learned from experimental studies of metal Fermi surfaces,[9] and it also followed from the band calculations of the states. From the theory one could see that the effect of the potential arising from the atoms was small because of the presence of deep electronic states, core states $|c>$, on each atom, which were otherwise

of little interest. In fact a rather good approximation to the Bloch function $|\psi_k>$ can be obtained from the free-electron plane-wave state $|\mathbf{k}>$ simply by orthogonalizing it to the core states,

$$|\psi_k> = |\mathbf{k}> - \Sigma_c |c><c|\mathbf{k}> \tag{3}$$

Corrections to this "orthogonalized plane-wave state" then could be calculated in terms of a *pseudopotential*, $W(\mathbf{r})$, which included not only the effect of the potential $V(\mathbf{r})$, arising from the atoms, but also a cancelling effect from the orthogonality,

$$W(\mathbf{r}) = V(\mathbf{r}) + \Sigma_c(\epsilon_k - \epsilon_c)|c><c| \tag{4}$$

The pseudopotential entered the theory of the Bloch electrons just like the true potential, but it was quite weak, as is illustrated in figure 3.

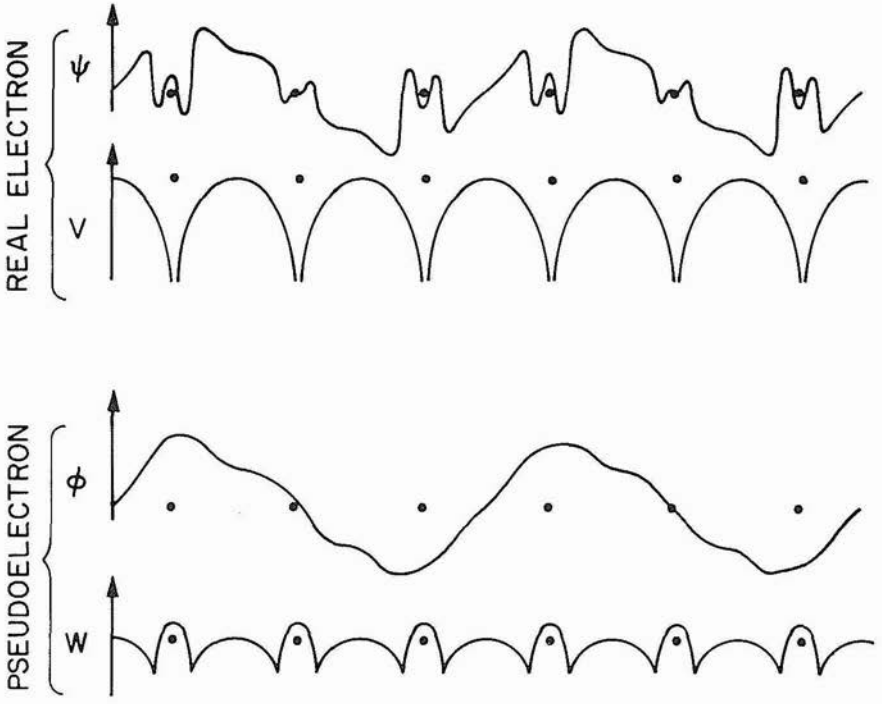

FIG. 3. IN THE UPPER FIGURE the potential V seen by the electrons in a metal is sketched, along with the Bloch state ψ, which describes the electron in the metal. In the figure below is a pseudopotential W, which differs from the potential V only near the nuclei. It is constructed so that the corresponding pseudowavefunction ϕ is exactly equal to the Bloch state except near the nucleus. The pseudowavefunction is simpler than the Bloch state, since it derives from a weak pseudopotential, but its energy and dynamical properties are the same.

The idea of a pseudopotential was not new. Fermi had first introduced it in the theory of collisions between protons and neutrons; however, that problem was sufficiently simple that the concept was not really needed. It had also been used by Phillips and Kleinman[11] to simplify band calculations for semiconductors. It is interesting that for semiconductors the smallness of the pseudopotential was not of importance, but the concept was useful in suggesting approximations that made the band calculation simpler without significant loss of accuracy. It could be used in a similar way to simplify the band calculations of metals, but in metals the smallness was of real utility.

Because the pseudopotential is weak, one may begin with the free-electron theory of Drude, using the quantum statistics as Sommerfeld had done, and directly calculate the corrections due to the pseudopotential. This made it immediately possible to estimate the entire range of properties of the metal,[12] including the electrical resistivity of the liquid metal. That resistivity came out to be very small, in accord with experiment, reflecting the weakness of the pseudopotential that describes the interaction between the electrons and the atoms in the metal, whether it be crystalline or liquid.

Pseudopotential perturbation theory was not limited to electrical properties, but allowed the calculation of the total energy of the metal as a perfect crystal, a distorted crystal, or one with crystalline defects. Thus it allowed calculation of the elastic properties, the vibration spectrum, and the energy of formation and properties of defects. This was the first state of condensed matter for which there existed a theory allowing the calculation of essentially all properties in terms of the basic electronic structure.

The essential step in this advance was the recognition that the effect of the electron-atom interaction could be used mathematically as a small correction, the concept of a weak pseudopotential. Theories have subsequently been developed that allow the calculation of the properties of most other types of solids in terms of the electronic structure.[13] It is interesting, however, that only in the case of the simple metals is the mathematical treatment of the ratio of the pseudopotential to the kinetic energy as the small parameter appropriate; in semiconductors, where pseudopotentials had been introduced earlier,[11] just the reverse is required, an expansion in the ratio of kinetic energy to the pseudopotential. The pseudopotential is a completely valid concept in all systems, but it is in the simple metals that it reduces an extremely intricate problem to one that is quite simple to understand and to calculate.

IV. MAGNETISM

Magnetism is a familiar property of special metals, such as iron, and at the time of Bloch's thesis it was recognized that it arose from the spin of the

metallic electrons. Bloch in fact showed[14] that in a standard approximation (the Hartree-Fock approximation) an electron gas at low enough density would become ferromagnetic. The physics of this analysis was essentially correct. Though the electronic structure in ferromagnetic metals is always much more complicated, his calculation can be redone using Bloch states for the metal crystal; it gives a good account of the perfect ferromagnetic state. This was first done in the sixties for nickel by Wakoh and Yamashita[15] and by Connolly.[16]

As in the problem of resistivity discussed in section III, the difficulty comes with the disordered system. If iron is heated above a critical temperature, the ferromagnetism is lost but the metal does not return to the usual nonmagnetic state. The magnetic properties are much like what would be expected if the electrons had frozen out on the atoms as Onnes had speculated[5] and the ferromagnetic state consisted of aligned electron spins on each atom that became disordered above the critical temperature. Such a disordered array of spins is quite inconsistent with Bloch states for the electrons. It suggested that in the ferromagnet the electrons must be localized, existing in qualitatively different kinds of states from the itinerant electrons of Drude and Bloch. This provides a simple description of ferromagnetism, but one which turns out not to apply to metals such as iron and nickel; measurements of the Fermi surfaces of these materials show "up-spin" and "down-spin" Fermi surfaces and little doubt that the electrons are itinerant. The paradox was resolved by Anderson's introduction of a *local moment* arising from itinerant electrons.[17] (This should not be confused with another well known part of Anderson's work concerning the true localization of electronic states in disordered systems.)

Anderson considered a single atom, such as iron, dissolved in a simple metal, such as copper. The magnetic electron states, $|d\uparrow>$ or $|d\downarrow>$ depending on spin direction, from the iron atom cannot freeze out an electron from the metal. They become what are called "resonant states," in which a passing electron may linger before moving on, just as a shopper may take one turn around a revolving door on the way into a store. This behavior is illustrated in figure 4. The analogy may be carried further to illustrate the local moment: The shopper could have gone to the right (counterclockwise) through the door, or to the left. A second shopper coming immediately after will find it much easier to go the same way as his predecessor. Thus for an extended period of time the door may be moving continually to the right as the shoppers flow in and out of the store, each taking one turn around on the way through. If we do not notice the difference between different shoppers, we may think one shopper is going round and round in a localized state as the others pass through.

The analogy with the local moment is immediate. An electron passing by may "resonate" at the iron atom and then move on. It might be an

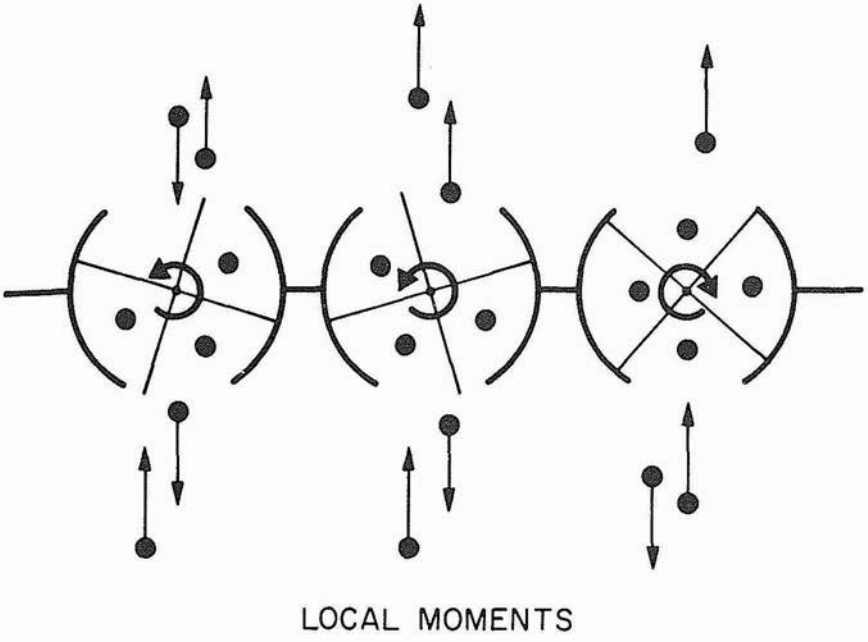

FIG. 4. THE FORMATION OF LOCAL MAGNETIC MOMENTS by itinerant electrons near an iron atom is analogous to the flow of people through a revolving door. Each may take a turn or two around on the way through, and if you cannot tell them apart, there is the same effect as if individuals were trapped there and the others went right through. Furthermore, if the first one goes to the right, corresponding to a magnetic moment directed into the plane of the figure, those that follow will tend to go the same way. In this way a ferromagnetic metal atom can acquire a long-lasting magnetic moment without holding any one electron an appreciable time.

electron of up-spin or down-spin, but if it is of up-spin, the next electron to resonate will more likely be up-spin (by the same physical mechanism that caused all electrons in Bloch's low-density electron gas to have the same spin), so that a local up-spin density is produced by the multitude of passing electrons. Since electrons are fundamentally indistinguishable, this is magnetically the same as if an up-spin electron had been condensed onto the atom, although the electrons' transport past the atom is as if they were all free.

An approximation to the resonant electron state can be made by adding some terms from the d-states of the free atom to each free-electron state. The form in which these enter, for electrons of up-spin for example, is

$$|\psi_{\mathbf{k}\uparrow}> \;=\; |\mathbf{k}\uparrow> + \frac{|d\uparrow><d\uparrow|V|\mathbf{k}\uparrow>}{\epsilon_{\mathbf{k}} - \epsilon_{d\uparrow}} \qquad (5)$$

The corresponding expression can be written immediately for down-spin. However, if this happens to be an up-spin resonance, the energy $\epsilon_{d\downarrow}$ is lower than $\epsilon_{d\uparrow}$ because of the other electrons of up-spin. The low value of $\epsilon_{d\downarrow}$ in Eq. (5) may enhance the resonance of this electron at the iron atom, cooperatively lowering the $\epsilon_{d\uparrow}$ for the other electrons; it adds its push to the revolving door.

This resonant electron state is not truly a Bloch state unless we construct a periodic array of such states with the same spin. Then each electronic state would have a well defined direction of spin, as in Bloch's states. However, we could make the corresponding array of iron atoms as far apart as we please and it is clear that the behavior of the system is that of rather independent "local moments" at each atom. If we think then in terms of these local moments, it is easy to understand how they may be disordered. We can, in fact, calculate the dependence of the energy upon the relative direction of moment on two atoms, the so-called "Ruderman-Kittel[18] interaction," which ultimately produces the ferromagnetic state once the iron atoms are quite close together.

The concept of the local moment enables us to transcend a difficult theoretical problem. The concept is extracted from the theory of an isolated spin and then used directly to study the multiple-moment system without worrying about the fact that the final disordered state we wish to discuss does not contain electron states of well-defined spin. Perhaps it is analogous to extracting the concept of "center of mass" from the string of beads and then calculating its simple parabolic trajectory although no bead is in itself undergoing such simple motion. We may even worry in that case about some approximation we made in specifying the interaction between different beads, but the center of mass transcends these details.

V. SUPERCONDUCTIVITY

I turn finally to the nature of a superconductor, which defied explanation for nearly fifty years after its discovery. It is interesting in the context of our discussion in section II that Landau and his colleague Ginsburg noted that an additional parameter, *the superconducting order parameter*, was needed to describe the superconducting state.[19] This violated the conditions necessary for the Fermi liquid theory, developed several years later and discussed in section II, to apply. This order parameter had a role in the theory of superconductivity very much like the role of spin ordering in the theory of ferromagnetism, but in the case of superconductivity the Ginsburg-Landau theory did not tell what the physical nature of this superconducting order was. It was known from other experiments (the isotope effect) that the origin of the state was related to the vibrations of the metal lattice, but the failure of the condition for the Fermi

liquid theory would suggest, correctly, that the superconducting state could not possibly be found by the perturbative techniques of quantum field theory. Perhaps this is why the nature of the state was so elusive. When it was finally revealed by Bardeen, Cooper, and Schrieffer,[20] the mathematical form of the energy in fact could not be written as an expansion in the interaction, confirming that the result was unobtainable by treating the interaction in perturbation theory.

The form of this BCS theory of superconductivity is intrinsically quite mathematical and difficult, though in the hands of the able theorist it is very accurate and very complete. Here we will discuss only one concept that makes it simple by transcending the details of the theory: this is the superconducting order parameter, introduced by Ginsburg and Landau, the nature of which was learned from the BCS theory. We do this first by analogy with a more familiar problem, that of radio-wave radiation from an antenna.

If we were to describe the radio antenna in terms of quantum theory, we would say that it emitted quanta of radiant energy, called photons, in all directions, as illustrated in figure 5. Then our home receiver is a photon

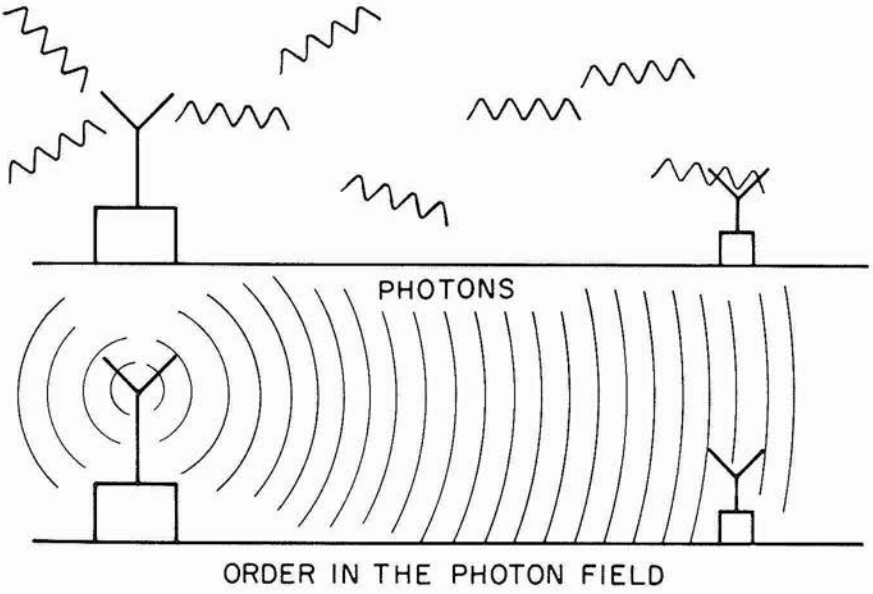

FIG. 5. IN QUANTUM THEORY a radio antenna can be considered as an emitter of photons that are collected by the radio receiver as shown in the upper figure. A slightly less accurate, but much simpler, description is obtained by introducing an electric field depending upon position and time, illustrated below. This electric field may be considered an order parameter in the photon field, and its definition requires one to abandon the idea of strict conservation of the number of photons.

collector, which detects the photons that come its way, unscrambles the time variation of the photon density, and produces the sound. This is a rigorous and exact treatment of radio communication, but, like the equations of motion of each bead, it is an extremely difficult way to get the answer. Any electrical engineer will instead define an electric field that varies in time and space and use Maxwell's Equations to estimate the resulting field on the home receiver, and finally he will deduce the sound intensity coming from the radio. What this engineer has done, in the context of our discussion here, is to introduce an order parameter (the electric field) in the gas of photons coming from the antenna. This approach is slightly less precise than the quantum theory, since in order to define the phase of the electric field we must give up the possibility of specifying the number of photons present, or the exact energy in the radiation field (a direct consequence of the Heisenberg Uncertainty Principle).

A more mathematical way of saying the same thing is to describe the state of radiation by specifying the number of photons of each wave number, $n(\mathbf{k})$, just as we specified the number of electrons (zero or one) in each electron state. Then we imagine a "creation operator" $a_{\mathbf{k}}^{+}$, which is defined so that the state $a_{\mathbf{k}}^{+}|n(\mathbf{k})>$ has $n+1$ photons in the state $\mathbf{k}$. Since $a_{\mathbf{k}}^{+}|n(\mathbf{k})>$ and $|n(\mathbf{k})>$ are different states of the photon system, one says that the average value of the operator $a_{\mathbf{k}}^{+}$ is zero. The electric field turns out to be proportional to the creation operator for photons, so it can have a nonzero average only if we discuss a state that has some probability of containing n photons and some probability of $n+1$ photons; that is, a state with an ill-defined number of photons. The state of the system must in fact be written as a sum, with coefficients u_n, of states $(a_{\mathbf{k}}^{+})^n\,|0>$ with many different numbers n of photons:

$$|\psi_{\mathbf{k}}> \;=\; \Sigma_n\, u_n (a_{\mathbf{k}}^{+})^n |0> \tag{6}$$

The u_n may be small except for n near the average value $\bar{n}$, but it must be nonzero over some range of n.

At first we might worry that we must talk of a state of uncertain energy, but on second thought we realize that the energy of the field from an antenna is so large that the uncertainties become negligible in comparison. It is customary under such circumstances to say that this is the classical limit or that quantum effects are negligible. This is the exact analogue to calculating the trajectory of a ball (or the necklace) and noting that if we specify exactly the position of the center of mass, the momentum becomes uncertain, but in the classical limit the uncertainty is negligible.

In the case of the superconductor, we learned from the BCS theory, and work following from it, that the order parameter is proportional to the product of two electron creation operators, one for electrons of up-spin and

one for electrons of down-spin. In its lowest energy state these electrons are to be moving in opposite directions so that, in analogy with Eq. (6), the BCS ground state uses a sum of terms $v_k a^+_{-k\downarrow} a^+_{k\uparrow}$ and u_k corresponding to the pair of states being occupied or empty, respectively. The BCS ground state is a product of such factors for each wave number,

$$|\psi_{BCS}> = \Pi_k(u_k + v_k a^+_{-k} a^+_k)\,|0> \tag{7}$$

The implications of this remarkable finding follow from the analogy with the antenna. We note first that the problem becomes much simpler because we relaxed any requirement of a fixed number of electrons. This is somehow much more difficult to accept than the relaxation of the requirement of a fixed number of photons, but it is much the same. For a reasonably sized superconductor, the uncertainty is extremely small compared to the total number of electrons. If two metallic specimens were connected so that electrons could flow between them, the number of electrons in each system would actually have corresponding uncertainties, and we know experimentally that it would not noticeably change the properties.

From this point of view the superconducting order parameter becomes a macroscopic classical variable, analogous to an electric field, which in this case is observable through superconducting currents that can be written in terms of it. In this regard also it introduces another variable in our electrical circuits; that variable is the phase difference of the order parameter that directly determines the current flow through a Josephson junction and must be included along with the voltage in solving for the current in the circuit. It is also a system parameter like the magnetization of iron that specifies the state of the metal.

Finally, it is fair to ask for the microscopic origin of the superconducting order, the analogy to the spin alignment in the case of ferromagnetism. The fact that it derives from a product of two creation operators, for up-spin and down-spin, means that it arises from pairs of electrons of opposing spins, called Cooper pairs. This clue to the origin came before the BCS ground state was found; Cooper[21] showed that the normal state of the metal could be lowered by forming one such pair; the difficulty then came in seeing that to make many Cooper pairs was simple only if electron conservation was relaxed. Then as long as the center of mass of each pair drifted at the same rate, it was possible to pair up essentially all of the electrons, with the electrons of each pair orbiting one another at such a large distance that each orbit crosses many others. Schrieffer[22] makes the analogy to pairs of dancers with each keeping track of his partner though they move in quite different parts of a crowded ballroom. This is possible for Cooper pairs only if the center of gravity of every pair is stationary, or if

they all drift together. In either case the coherent motion, or lack of motion, of the Cooper pairs is exactly what is represented by the order parameter. It is also what prevents a superconducting current, once set in motion, from being dissipated by individual electrons colliding with defects in the crystal (see figure 6).

As with the center of mass, the quasiparticle, the pseudopotential, and the local moment, the superconducting order parameter is not necessary to the understanding of the phenomenon, but is an insight that can suddenly make the phenomenon seem simple and therefore understandable. Whether these concepts be inventions or discoveries, they are, in my view, the highest achievements of the theory of metals in the fifty years since Bloch's introduction of Bloch states to the theory.

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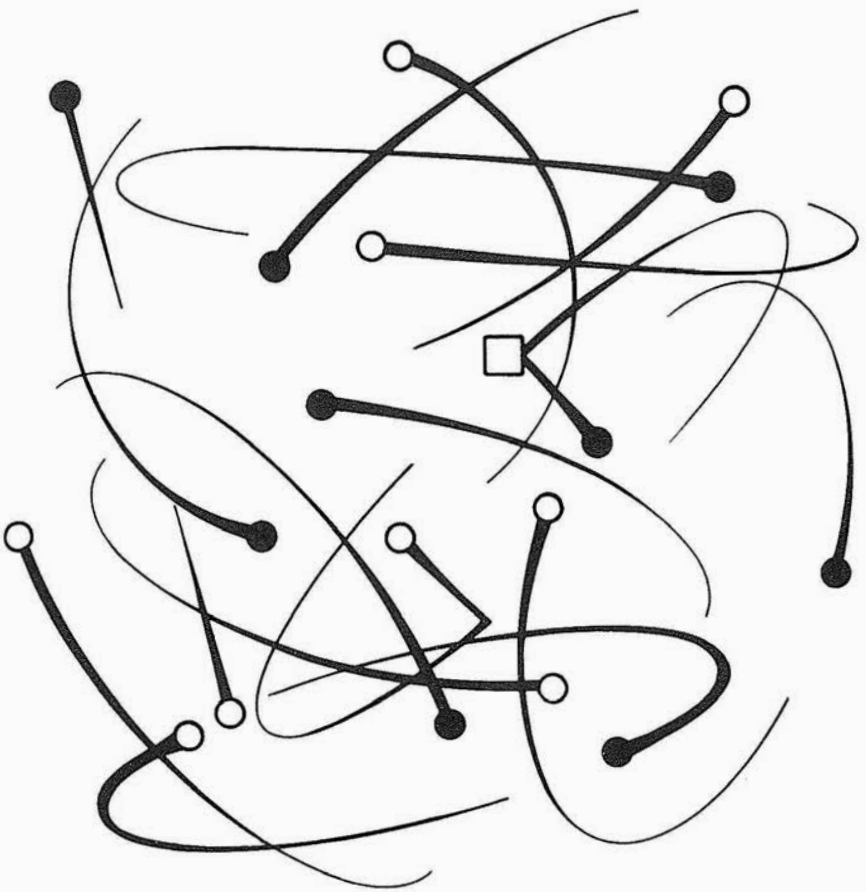

FIG. 6. THE SUPERCONDUCTING STATE arises from a subtle ordering of the electrons in which they form pairs rotating around each other, so that the center of mass of every pair drifts exactly together. In the figure each empty circle is at the opposite diameter of its orbit as a filled circle moving in the same orbit. Thus if a current is flowing, the collision of one electron with an obstacle, here an impurity drawn as a square, will cause its partner to be deflected also, without reducing the total flow of current. The definition of the corresponding order parameter requires the relaxation of strict electron conservation in analogy with the introduction of the electric field in figure 5.